493 VOLUME 80 SEPARATE No. 493

PROCEEDINGS

AMERICAN SOCIETY
OF
CIVIL ENGINEERS

SEPTEMBER, 1954

WASTE DISPOSAL AT A STEEL PLANT: TREATMENT OF SHEET AND TIN MILL WASTES

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SANITARY ENGINEERING
DIVISION

{Discussion open until January 1, 1955}

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Printed in the United States of America

Headquarters of the Society
33 W. 39th St.
New York 18, N. Y.

PRICE $0.50 PER COPY

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This paper was published at 1745 S. State Street, Ann Arbor, Mich., by the American Society of Civil Engineers. Editorial and General Offices are at 33 West Thirty-ninth Street, New York 18, N. Y.

WASTE DISPOSAL AT A STEEL PLANT: TREATMENT OF SHEET AND TIN MILL WASHES

Hugh MacDougall[1]

Introduction

The volume of waste originating in the Sheet and Tin Mill of the Fairless Works is very small. A total of 55,000 gpm. will receive treatment, but of this amount, only 3,000 gpm. is discharged from the Sheet and Tin Mill.

However, in terms of variety of wastes, the Sheet and Tin Mill far exceeds all other parts of the Works and the treatment problem was correspondingly complex. It was therefore decided to build a treatment plant in the Sheet and Tin Mill area and treat the wastes originating there separately before combining the relatively small flows with the much larger flows from other sources.

The function of the Sheet and Tin Mill is to produce Sheet steel and tin plate from the raw strip coils rolled in the Hot Strip Mill. In the process, the steel is pickled, cold rolled, annealed, tempered and coated. Each production facility produces its particular wastes.

Description of Wastes

Fig. 1 is a composite chart which shows the types of liquid wastes and the production facilities from which they originate. The main constituents of the wastes and their origins may be summarized as follows:

Acid Wastes	
1. Sulphuric Acid	80-inch Pickler Electrolytic Tinning
2. Hydrochloric Acid	Hot Dip Tinning Tin House Laboratory
3. Chromic Acid	Electrolytic Tinning
Alkaline Wastes	
1. Sodium Orthosilicate	Electrolytic Tinning Continuous Cleaning Continuous Annealing Hot Dip Tinning
2. Soda Ash	Hot Dip Tinning

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Oils

1. Soluble (Emulsions)	4 Stand Mill (5 Stand Mill Alternate) Roll and Machine Shop Precipitron Bumps
2. Insoluble (Floating)	5 Stand Mill Mill Sumps

Sulphuric acid wastes include spent pickling solution and acid rinse water. The spent pickling solution contains about 6% free acid and 15% ferrous sulphate. Rinse water and fog removal water contain small quantities of free acid estimated at .035%.

Hydrochloric acid rinse water contains dilute acid. A small quantity of more concentrated acid is discharged infrequently by the tin house laboratory.

Chromium wastes contain sodium dichromate and sodium acid phosphate in dilute quantities which are carried over in rinsing operations.

Sodium orthosilicate cleaning solutions are encountered, having a concentration estimated at 3% to 12%. Rinse water contains traces of alkalinity.

Soluble oil rolling solutions contain emulsions of animal oil, some palm oil, and small amounts of iron oxide. To this are added waste grinding and coolant solutions which also contain animal oil in emulsified form. Continuous flows have only small percentages of these impurities gained in rinsing operations, but when tanks are cleaned, the wastes may contain as much as 10% oil. Discharges from precipitron sumps also contain emulsified oil washed from the precipitrons during cleaning.

Insoluble or floating oils are derived chiefly from rolling operations using palm oil. The continuous discharge from the 5 Stand Mill skimmer tank may carry about 20 p.p.m. palm oil. Intermittent discharge may contain 70% palm oil, plus insolubles and water. In addition to palm oil, small quantities of other floating oils such as lube oils and greases reach the plant from floor sumps.

Waste Quantities

At the time of writing, some of the facilities in the Sheet and Tin Mill have operated only on an experimental and intermittent basis and all the design data has not been verified during continuous normal operation. However, as the plant is designed to provide considerable flexibility, procedures may be adapted to treat the wastes properly as the various elements of the mill go into full production.

The largest flows reaching the plant are the continuous discharges carrying oil from the 4 and 5 Stand Mills, estimated at 1,000 gpm. each, which make up 2/3 of the total design flow. Of the balance, 700 gpm. is alkaline rinse water and about 200 gpm. is acid rinse water. Another smaller but very important continuous discharge is the spent pickling solution which averages about 30 gpm.

Intermittent discharges reach the plant when spent solutions are discharged by the various production facilities. In comparison to the total flows these are comparatively small in total volume. However, they are considered of primary importance in the design of the treatment facilities.

Principles of Design

In the design of the treatment plant, certain fundamental principles were followed. These are:

a. Wastes are segregated according to type and delivered to the treatment plant through independent pipelines in order that each waste may be used to the best advantage in the treatment process. Fifteen pipes enter the plant carrying waste waters from the various production units.
b. Intermittent flows of high concentration are temporarily stored and then "bled" slowly into the continuous flows in order to maintain as uniform conditions as possible.
c. As far as possible, wastes are combined in the treatment process to neutralize each other or to assist in the removal of other impurities.
d. Treatment processes are those which have been successfully applied under similar circumstances.
e. Designs incorporate equipment which was available from a number of manufacturers.
f. Wherever possible the equipment is automatically controlled and operation is performed by a minimum of skilled help.

Principles of Treatment

In general, all polluting material must be changed to a liquid or a solid form which will either rise to the surface, or will settle out of the water in which it is carried. This involves both mechanical and chemical treatment after which the water must be kept in a quiet state to permit the rising or settling action. Each type of waste is therefore, subjected to a particular process before it is clarified by gravity.

Insoluble Oils

These include palm oil, lubricating oils and greases which are not emulsified and are carried along in the waste flow as globules of free oil which will float to the surface in quiescent water and there coalesce into an oil sheet. The oil separator is the standard piece of equipment for this type of treatment and is widely used in the oil industry. Oil carrying water flows slowly through a primary and secondary chamber allowing sufficient time for the oil to rise to the surface. The oil sheet is then skimmed off. Sediments in the water sink to the bottom and are removed by collectors.

Soluble Oils

In certain roll solutions, grinding solutions, and machine shop coolants, oil occurs in varying degrees of emulsification. The oil is in a finely divided or colloidal condition in which the oil particles are so small that they remain in suspension and will not float to the surface. Moreover, they are prevented from coalescing by emulsifying agents and possibly by electrostatic charges. To remove such oils two methods are employed. In the first, the emulsions are "broken" by the addition of acid which causes the colloidal oil particles to merge into globules large enough to float. The second method provides a chemical precipitate by which the oil will be absorbed and then be removed by sedimentation or floatation. In this plant, the two processes are combined to produce an oil free effluent. The use of spent pickling solution and sodium orthosilicate waste contributes to both of these processes. The acid content of spent pickling solution is used to lower the pH and break the emulsions.

Following this treatment, waste sodium orthosilicate plus milk of lime are added. These neutralize the sulphuric acid and also combine with ferrous sulphate content of the spent pickling solution.

Three practically insoluble compounds are produced; namely, calcium sulphate ($CaSO_4$), ferrous hydroxide ($Fe(OH)_2$) and silicic acid (H_4SiO_4). Sodium sulphate (Na_2SO_4) is also formed, but being quite soluble, under these conditions it all goes into solution.

The insoluble compounds form precipitates which tend to settle out of the water. This process is assisted by gently stirring the mixture in a flocculating chamber where the particles adhere together in larger clusters. After leaving the flocculating chamber the water enters a clarifying chamber and the "floc" settles carrying with it other finely divided impurities and some absorbed oil. The balance of the oil rises and is skimmed off the surface. The whole treatment process closely resembles a commonly used method for removing turbidities in water supplies in which ferrous sulphate is added as a flocculating agent.

As may be seen from the above description, the removal of soluble oil is a two stage process. In the first, the oily wastes are acidified to a pH between 5 and 6. In the second, alkaline wastes plus lime are added to raise the alkalinity to a pH between 9 and 10. Thus, other wastes become effective agents in the removal of soluble oils.

Acid Wastes

One of the most perplexing problems in the steel industry is the disposal of spent sulphuric acid after the pickling of steel products. Sulphuric acid is used for the removal of iron oxide scale from hot rolled products prior to cold reduction. Pickling is in part a chemical process in which some iron is attacked by the acid to form ferrous sulphate. As the ferrous sulphate content of the acid builds up, a concentration is finally reached where the pickling action is inhibited and the spent pickling solution must be disposed of. Depending on the process used in pickling, the spent pickling solution contains 2 to 7% free acid and 15 to 22% ferrous sulphate.

At the Fairless Works, spent pickling solution is transported from the plant by tank truck for further processing elsewhere. However, an acid neutralization plant has been built as a part of the Sheet and Tin Mill Waste Treatment Plant to be used only in the event of unforeseen contingencies.

Acid rinse waters from the electrolytic tinning line is used in the soluble oil treatment described above. In addition, spent pickling solution is also required in this process and some also is employed in the reduction of chromium waste.

Alkaline Wastes

Alkaline wastes fit very conveniently into the composite treatment process. After passing through the acid stage, the pH of soluble oil wastes must be raised to neutralize free acid and to form insoluble hydroxides of the metallic wastes. Although lime is required to complete these reactions, some saving can be made by employing the sodium orthosilicate waste to neutralize the free sulphuric acid. An insoluble precipitate is thus formed which flocculates readily and assists the final clarification of the soluble oil wastes. Thus the alkaline wastes became effective agents in the treatment process.

Chromium Wastes

Chromium compounds are used in many metal working and finishing plants. Rinse waters containing chromium or spent chromic acid solutions are therefore of frequent occurrence in industrial wastes and there is a considerable background of experience in their treatment. In the hexavalent form chromium salts are highly toxic and most state regulations insist on their removal before the wastes are discharged into public water supplies.

The standard practice appears to be to adjust the pH to 4.5 or below with sulphuric acid, reduce the hexavalent chromium to trivalent chromium with a reducing agent such as sulphur dioxide, sodium bisulphite or ferrous sulphate and then to precipitate the chromium as hydroxide by the addition of lime.

At the Fairless Works the obvious reducing agent to employ is the ferrous sulphate which is contained in spent pickling solution. The residual sulphuric acid in the spent pickling solution is also useful in lowering the pH of the chromium solution. After the reduction of the hexavalent chromium, the treated waste is combined with the other flows and milk of lime is added to complete the total reaction.

In addition to chromium waste, rinse water from the electrolytic tinning process contains sodium acid phosphate which can also be eliminated by treatment with spent pickling solution and lime. The end products formed by the combined treatment of chromates and phosphates are chromium and iron hydroxides, calcium and sodium bisulphate and ferrous phosphate. With the exception of sodium bisulphate, all these products are practically insoluble and are precipitated in the clarifier.

Description of Treatment Plant

The Sheet and Tin Mill Wastes Treatment Plant actually consists of four integrated sections, each with its specific function. These are:

1. Oil Interception
2. Chromium Wastes Pre-Treatment
3. Spent Pickling Solution Storage and Handling
4. Emergency Acid Neutralization

Oil Interception

The Oil Interception Plant comprises three basic structures: The Separator, the flash mixer and the flocculator-clarifier, plus holding and storage tanks and pumping equipment. Wastes from either the 4 or 5 Stand Mills containing small quantities of floating oils, such as palm oil and lube oils, are pumped directly to the separator. This is a standard two stage design, sub-divided into two primary and two secondary compartments which provide forty minutes detention for a design flow of 3,000 gpm. A picture of the separator is shown on Fig. 2. Floating oils are skimmed and pumped automatically to a 24,000 gallon elevated storage tank. Sludge is scraped to sumps in each compartment where helical cross collectors move it to telescoping valve connections. After manual withdrawal, the sludge is pumped automatically to a sludge lagoon. When palm oil rolling solution tanks are dumped, the waste oil is held in a 42,000 gallon tank to permit the palm oil to separate. From this tank, the aqueous portion is withdrawn to the separator and the oil is pumped to a 24,000 gallon elevated storage tank.

All soluble oil wastes and acid rinse water pass through the flash mixer where waste pickle liquor is added to crack the emulsions. The mixer is constructed of concrete with an acid proof brick lining, and it is equipped with a 3,500 gpm. mixer located in a central well as shown in Fig. 3. Here, 28 minutes detention is provided for a design flow of 1,200 gpm. The flow is discharged over a peripheral weir and after the addition of the alkaline wastes, plus mile of lime, the combined flows enter the central well of the flocculator-clarifier illustrated in Fig. 4. Here, two vertical mixers complete the blending of the acid and alkaline constituents of the wastes.

The flow then passes through the flocculating and settling chambers and is discharged over a peripheral weir. A total detention time of one and 3/4 hours is provided for a design flow of 2,000 gpm. Sludge is collected to a central sump and withdrawn through a telescoping valve into a sludge chamber from which it is automatically pumped by rotary displacement pumps to the sludge lagoon. Skimmed oil is discharged to an oil sump and then automatically pumped to a 24,000 gallon elevated storage tank.

The effluent from the flocculator-clarifier is combined with the floating oil wastes entering the oil separator and after further clarification in the separator, it is discharged to the industrial wastes sewers leading to the Terminal Treating Plant located at the river site.

Chromium Wastes Pre-Treatment

The equipment for this operation consists of two 1,500 gallon reaction tanks, a 6,000 gallon holding tank for concentrated chromium wastes, a 1,500 gallon storage tank for spent pickling solution and a pump type chemical feeder. One reaction tank is shown on Fig. 5. Chromium contaminated rinse water enters the reaction tanks through a 3-inch rotameter. Spent pickling solution is added to the wastes at a pre-determined rate and the hexavalent chromium solution is retained an hour to carry the reduction reaction to completion. Mixers are provided in the reaction tanks.

Concentrated chromium wastes are fed slowly from the holding tank to the reaction tanks through a 1/2 inch rotameter.

After treatment, the chromium wastes are combined with other flows entering the flocculator-clarifier where the chromium is precipitated as an insoluble hydroxide.

Spent Pickling Solution Storage and Handling Plant

A total storage capacity of 400,000 gallons has been provided for spent pickling solution in two steel tanks which are acid-proofed with rubber membrane and brick, as illustrated in Fig. 6. All spent pickling solution is pumped to these tanks. Located in an underground chamber adjacent to the tanks are four acid-proof pumps which can withdraw the spent pickling solution from either tank. Two of these pumps, each with a capacity of 50 gpm, may be used to pump to the oil interception plant or to the acid neutralization plant. The other pumps, each having a capacity of 150 gpm, are used to pump the spent pickling solution to the truck loading station. These arrangements permit the disposal of the spent pickling solution either in the waste treatment process, by neutralization or by trucking to an outside destination.

Emergency Acid Neutralization Plant

The acid neutralization plant is designed to neutralize the entire spent pickling solution production in the event of unforeseen contingencies. The plant consists of lime storage and slaking equipment, reaction tanks and sludge pumping equipment. Fig. 7 is a view of the lime plant.

In practice, the spent pickling solution is pumped from the storage tanks through a 2-1/2 inch rotameter into the first of four wooden tanks, each 10 feet in diameter, with a capacity of 4,700 gallons. The tanks are connected in series and arranged for gravity flow through the series. Milk of lime is also added in the first tank through a 3 inch rotameter. Each tank is equipped with a mixing paddle to assist the reaction and keep the contents in suspension.

From the final tank, the neutralized effluent overflows to the suction of a duplex plunger type sludge pump having a capacity of 200 gpm. In order to provide this flow to the pump and to dilute the sludge to a more fluid condition, a float controlled water supply is furnished in the fourth tank. All the neutralized effluent is pumped to the sludge lagoon.

As the neutralization process involves the reaction of the ferrous sulphate content of the spent pickling solution with the milk of lime, considerable time is required to complete the reaction. For this reason, a detention time of two hours is provided for a total flow of 150 gpm.

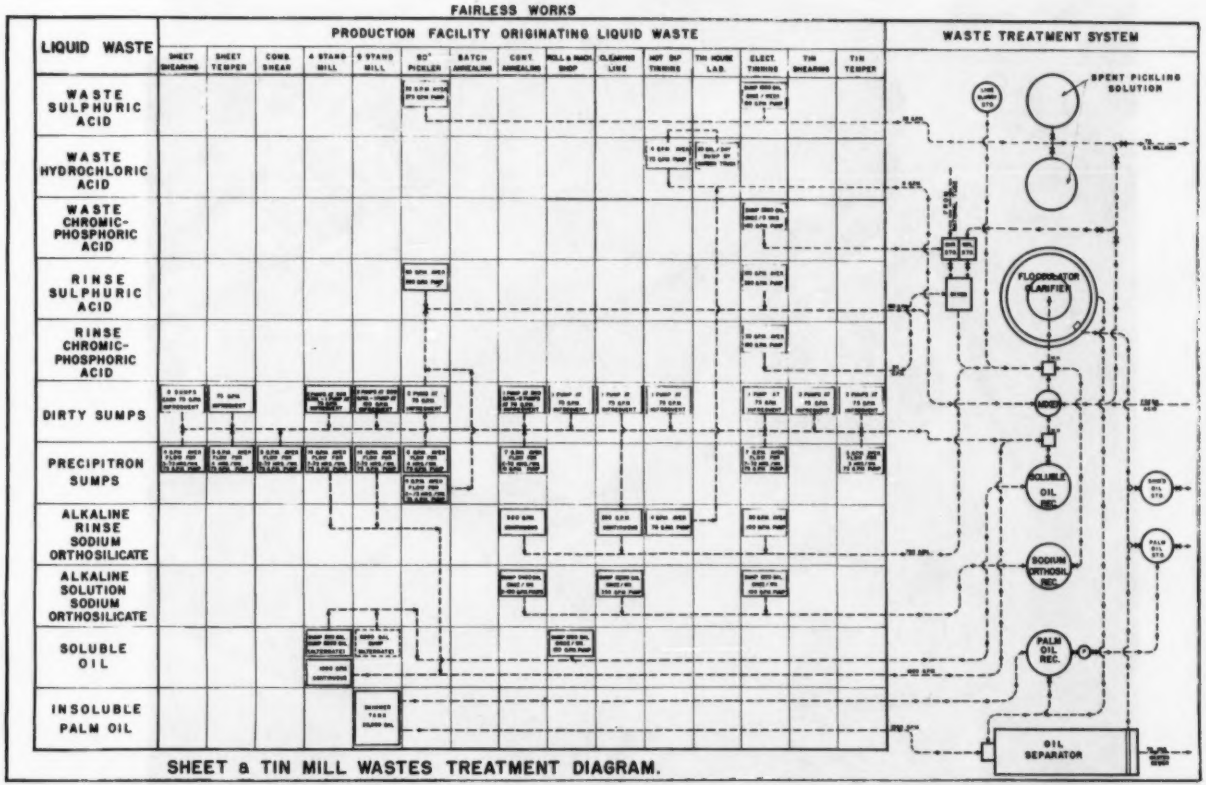
Milk of lime required for the neutralization process and other phases of treatment is obtained by slaking high calcium quicklime. The slaker is fed by a belt type gravimetric feeder rated at 2500 pounds per hour, which is supplied from a 150 ton storage bin. The lime feeding and slaking operation is automatically controlled by a float switch located in a milk of lime sump, from which the lime is pumped to the neutralization plant.

Treatment Control

Operators of the treatment plant have been taught to control the treatment process by maintaining the pH of the wastes between certain levels at critical points in the process. This they do with pH colorimetric paper. In the oil emulsion cracking phase, spent pickling solution is added until the pH drops to 5. In the clarifier, milk of lime is added until the pH rises above 9. Chromium wastes are pre-treated with spent pickling solution at a pH of 4. Experience in observing the quality of the floc formation and the quality of the effluent is also of value in controlling treatment.

Results of treatment are assessed by periodic sampling and testing of the plart effluent. Analyses are also made of the chromium wastes and of the spent pickling solution. Although the plant has been in operation for a relatively short period, the results to date have been satisfactory.

Oil, grease, color, hexavalent chromium and phosphate are being removed. The treated waste leaves the plant with a high pH due to the calcium hydroxide content. This might be reduced somewhat if the Sheet and Tin Mill Plant were a totally independent unit. However, as the effluent of the plant is combined with other wastes receiving treatment at the Terminal Treatment Plant, the excess alkalinity is valuable there in that it raises the pH of the total waste discharge and thus helps in the final clarification process.



SHEET & TIN MILL WASTES TREATMENT DIAGRAM.

Fig. 1

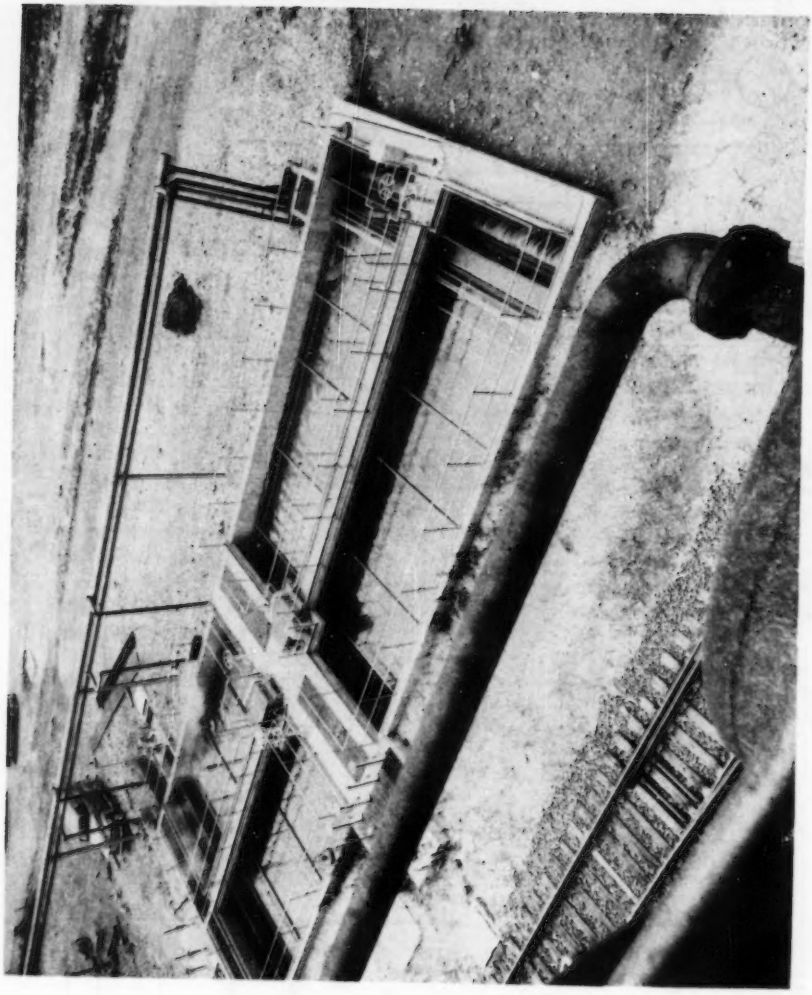


Fig. 2—API Separator

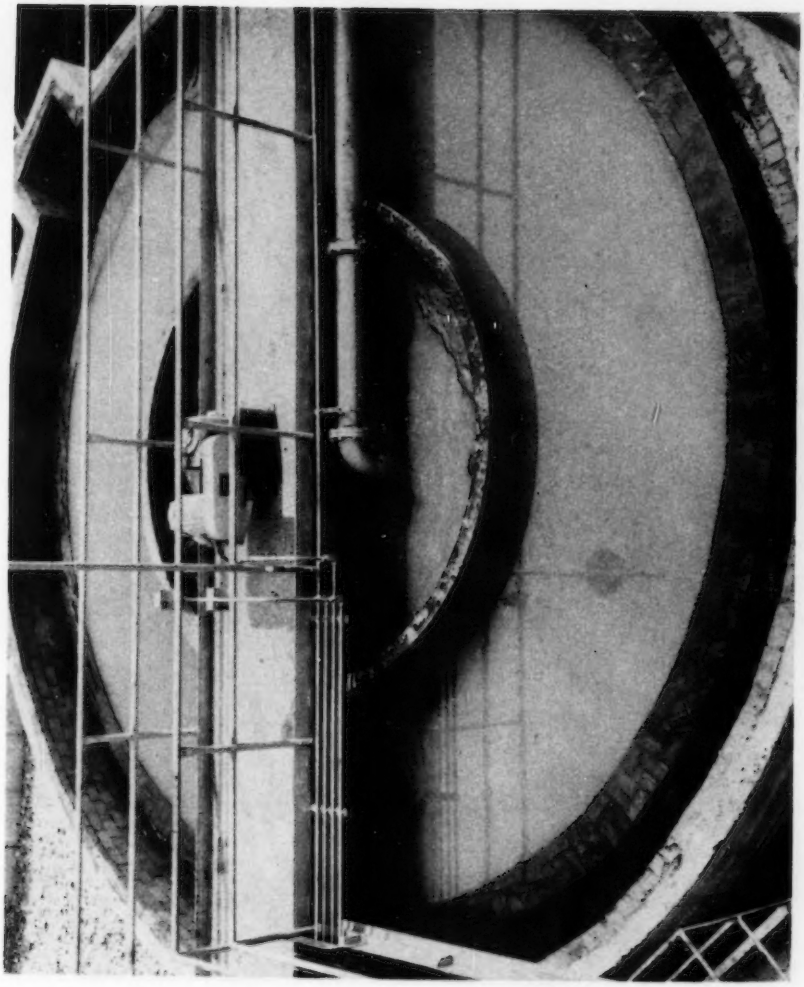


Fig. 3—Flash Mixer

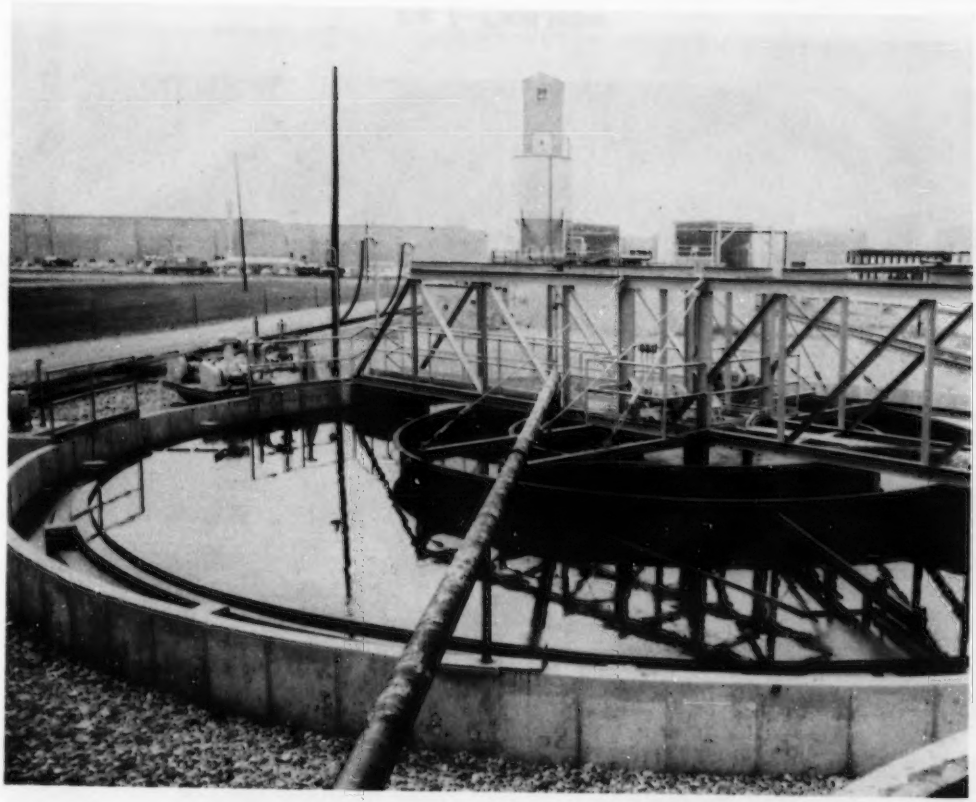


Fig. 4—Flocculator-Clarifier

Fig. 5—Chromic Acid Waste

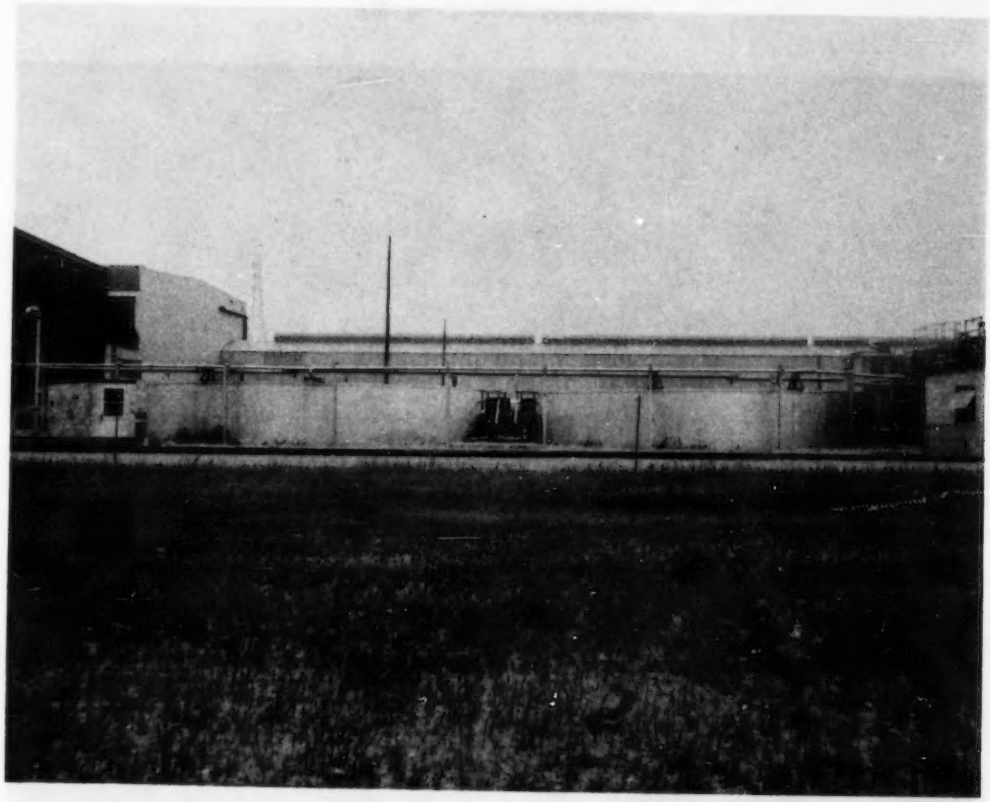


Fig. 6—Waste Pickle Liquor Storage Tanks

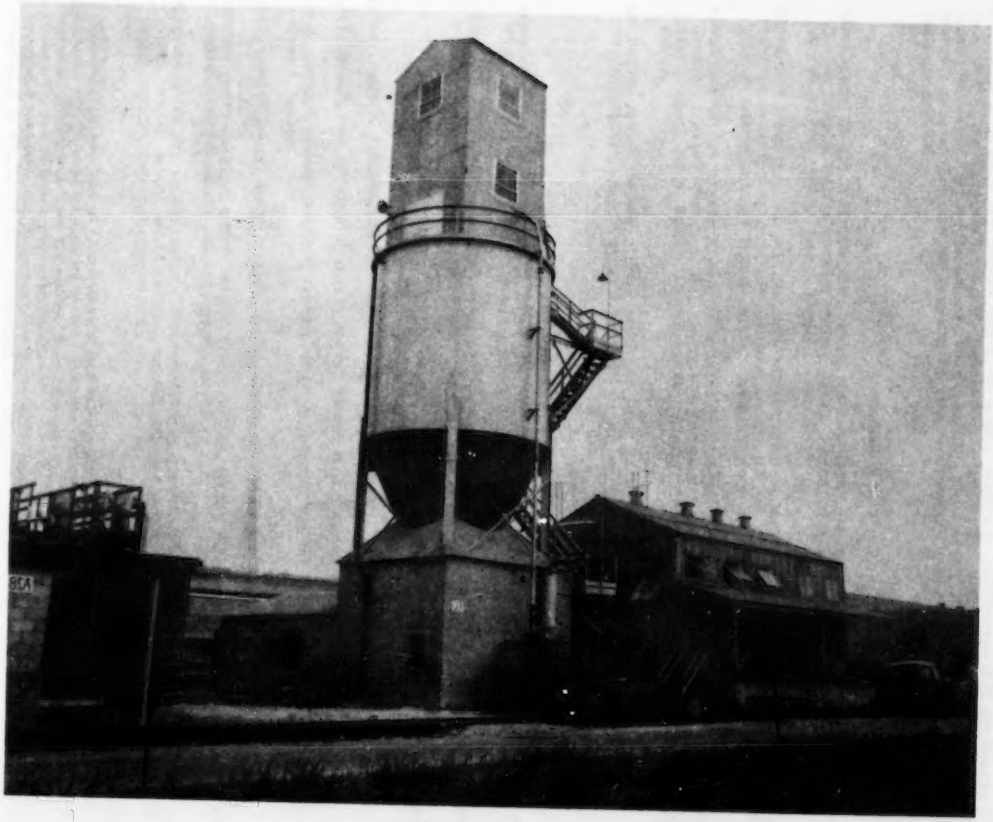


Fig. 7—Lime Storage and Slaking Plant

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The technical papers published in the past year are presented below. Technical-division sponsorship is indicated by an abbreviation at the end of each Separate Number, the symbols referring to: Air Transport (AT), City Planning (CP), Construction (CO), Engineering Mechanics (EM), Highway (HW), Hydraulics (HY), Irrigation and Drainage (IR), Power (PO), Sanitary Engineering (SA), Soil Mechanics and Foundations (SM), Structural (ST), Surveying and Mapping (SU), and Waterways (WW) divisions. For titles and order coupons, refer to the appropriate issue of "Civil Engineering" or write for a cumulative price list.

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a. Presented at the New York (N.Y.) Convention of the Society in October, 1953.
b. Beginning with "Proceedings-Separate No. 290," published in October, 1953, an automatic distribution of papers was inaugurated, as outlined in "Civil Engineering," June, 1953, page 66.
c. Discussion of several papers, grouped by Divisions.
d. Presented at the Atlanta (Ga.) Convention of the Society in February, 1954.
e. Presented at the Atlantic City (N.J.) Convention in June, 1954.

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